

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 December 2002 (19.12.2002)

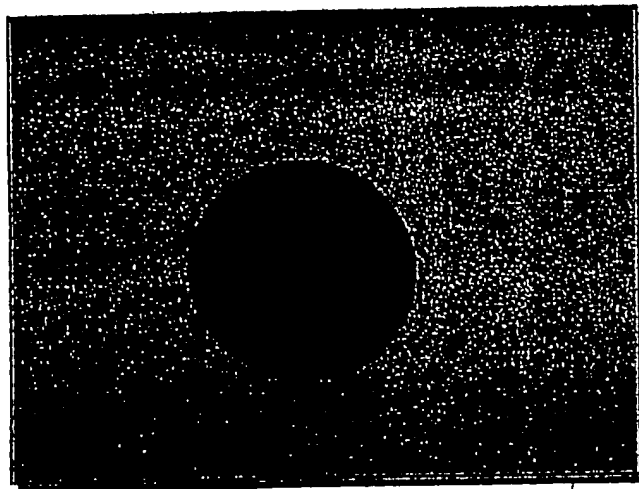
PCT

(10) International Publication Number
WO 02/100775 A2

- (51) International Patent Classification⁷: C01B 31/00 (74) Agent: THOMPSON, Alan, H.; P.O. Box 808, L-703, Livermore, CA 94551 (US).
- (21) International Application Number: PCT/US02/18669
- (22) International Filing Date: 11 June 2002 (11.06.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/298,602 13 June 2001 (13.06.2001) US
10/163,720 5 June 2002 (05.06.2002) US
- (71) Applicant: THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 1111 Franklin Street, Oakland, CA 94607-5200 (US).
- (72) Inventors: TILLOTSON, Thomas, M.; 210 E. Berverdor Avenue, Tracy, CA 95376 (US). ANDRESEN, Brian, D.; 1075 Alison Circle, Livermore, CA 94550 (US). AL-CARAZ, Armando; 592 Chardonnay Drive, Fremont, CA 94539 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: CARBON NANOTUBE COATINGS AS CHEMICAL ABSORBERS



(57) Abstract: Airborne or aqueous organic compound collection using carbon nanotubes. Exposure of carbon nanotube-coated disks to controlled atmospheres of chemical warfare (CW)-related compounds provide superior extraction and retention efficiencies compared to commercially available airborne organic compound collectors. For example, the carbon nanotube-coated collectors were four (4) times more efficient toward concentrating dimethylmethyl-phosphonate (DMMP), a CW surrogate, than Carboxen, the optimized carbonized polymer for CW-related vapor collections. In addition to DMMP, the carbon nanotube-coated material possesses high collection efficiencies for the CW-related compounds diisopropylaminoethanol (DIEA), and diisopropylmethylphosphonate (DIMP).

WO 02/100775 A2



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

CARBON NANOTUBE COATINGS AS CHEMICAL ABSORBERS

(0001) The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

RELATED APPLICATION

(0002) This application relates to U.S. Provisional Application No. 60/298,602 filed June 13, 2001, and claims priority thereof.

BACKGROUND OF THE INVENTION

(0003) The present invention relates to the collection of airborne or aqueous organic compounds, particularly to the collection of chemical warfare (CW)-related compounds, and more particularly to a collector for such organic compounds which is provided with carbon nanotubes whereby extraction and retention efficiencies is greatly increased over conventional airborne or aqueous compound collection approaches.

(0004) Since the accidental discovery of carbon nanotubes about a decade ago, carbon nanotubes have displayed a considerable number of unique properties. Researchers have found carbon nanotubes to be stronger and tougher than steel, capable of carrying higher current densities than either copper or superconductors, and able to form transistors only a few nanometers wide. Unlike diamond and graphite, which are both insulators, a remarkable property of carbon nanotubes is their ability to act as either a metal or semiconductor. Applications range from future ultrasmall electronic circuits, to ultrathin CRTs, to bullet proof armor, gas storage, air filter units, etc. In addition, the carbon nanotubes can be doped so as to absorb hydrogen, for example, with a sorption-desorption cycle than can be repeated with little decrease in the sorption capacity.

(0005) Derived from spheroidal fullness ("Buckyballs"), a carbon nanotube is a long and hollow array of hexagonal-pattern carbon atoms.

Similar to a single layer of graphite rolled into a tube, carbon nanotubes are typically 2nm in diameters and several hundred micrometers long.

(0006) While carbon nanotubes have been considered for many applications, as pointed out above, little prior effort has been focused on the chemistry of the carbon nanotubes as collectors and concentrators of target compounds in air, water, or waste streams. The present invention is directed to utilizing carbon nanotubes as collectors and concentrators of organic compounds in air, water, or waste streams, particularly CW-related vapor collections and concentrations, such as CW surrogates dimethylmethylphosphonate (DMMP), diisopropyl-aminaethanol (DIEA), and diisopropylmethylphosphonate (DIMP).

SUMMARY OF THE INVENTION

(0007) It is an object of the present invention to provide carbon nanotube coatings as chemical absorbers.

(0008) A further object of the invention is to provide airborne or aqueous organic compound collectors and concentrators utilizing carbon nanotubes.

(0009) A further object of the invention is to provide collectors for airborne chemical warfare-related compounds using carbon nanotubes.

(0010) Another object of the invention is to provide organic compound collectors having carbon nanotubes.

(0011) Another object of the invention is to provide carbon nanotube coatings on an airborne organic compound collector.

(0012) Another object of the invention is to provide an airborne collector with a carbon nanotube coating for collecting and concentrating chemical warfare-related organic compounds.

(0013) Other objects and advantages of the invention will become apparent from the following description and accompanying drawing. Basically, the present invention involves providing an airborne or aqueous organic compound collector with a coating of carbon nanotubes. Collectors using carbon nanotubes have been shown to be four-ten times more effective

toward concentrating a chemical warfare (CW) surrogate than the currently utilized optimized carbonized polymers, such as Carboxen made by Sepelco (Aldridge/Sigma), for CW-related vapor collections.

(0014) The carbon nanotubes, as pointed out above, are typically 2nm in diameter and several hundred micrometers long, and can be coated on a metal substrate, which for example, may be a disc or honeycomb, made of metal, plastic, and ceramics by suspending the nanotubes uniformly in a solvent containing a binder, for example, an organosilane such as polydimethylsilane, and then applying such to the substrate via ultrasonic impulses to a spray apparatus. More simply, but less effectively, a substrate, such as a 1cm metal disk can be uniformly airbrushed with a solution containing the carbon nanotubes. Exposure of the carbon nanotube-coated disks to controlled atmospheres of CW-related compounds revealed very superior extraction and retention efficiencies compared to the currently utilized Carboxen.

BRIEF DESCRIPTION OF THE DRAWINGS

(0015) The accompanying drawings, which are incorporated into and form a part of the disclosure, illustrates an embodiment of the invention and test results thereof and, together with the description, serve to explain the principles of the invention.

(0016) The single figure is a view of an embodiment of a collector disk with a coating of carbon nanotubes.

DETAILED DESCRIPTION OF THE INVENTION

(0017) The present invention is directed to carbon nanotube coatings as chemical absorbers, and particularly for the collection and concentration of chemical warfare (CW)-related airborne organic compounds. A carbon nanotube, derived from spheroidal fullness ("Buckyballs") is a long and hollow array of hexagonal-pattern carbon atoms. Similar to a single layer of graphite rolled into a tube, the carbon nanotubes are typically 2nm in diameter and several hundred micrometers long. The carbon nanotubes may

be prepared, for example, by applying a direct-current arc discharge (18 to 35V and 100 to 200 Ω), typically from an arc welder, between two graphite electrodes in an inert atmosphere.

(0018) To experimentally verify the invention, the previously formed pure carbon nanotubes were then coated on a uniform 1-cm metal disk by two methods. The first method, most simple but least effective, was airbrushed uniformly with a solution of the carbon nanotubes. However, the coatings were not fully uniform. The second method, which was uniformly effective, involved suspending the carbon nanotubes uniformly in a solvent containing polydimethylsilane as a binder, and then applying ultrasonic impulses to the spray apparatus while spray coating 1-cm metal disk.

(0019) The drawing illustrates an embodiment of the collector generally indicated at 10 and composed of a substrate or disk 11 coated with carbon nanotube 12. For comparison, we coated a single standardized 1-cm metal disk with an identical weight of Carboxen, a commercially air-filtration medium with very high collection efficiencies that is the optimized carbonized polymer for collecting CW-related vapors.

(0020) We then exposed the coated disks to a controlled atmosphere containing three (3) CW surrogates; dimethylmethylphosphonate (DMMP), diisopropylaminoethanol (DIEA), and diisopropylmethylphosphonate (DIMP). To quantitatively measure airborne-collection efficiencies, we used solid-phase microextraction (SPME) and gas-chromatography mass spectrometry (GC-MS) to obtain weight-per-weight comparisons. This clearly established that the carbon nanotube-coated disks possessed high collection efficiencies. In fact, we found that the carbon nanotubes were four (4) times more efficient than Carboxen in extracting, concentrating, and retaining one of the surrogates-DMMP, which is a significant advance in the art.

(0021) The GC-MS measurements taken established retention times and identification of the three target compound: DMMP (at 5.7 min.); DIMP (at 9.9 min.) and DIEA (at 9.5 min.) which were collected as fugitive air emissions

using carbon nanotube technology. The concentrations of the collected target compounds also far exceeded commercial polymeric materials, such as Carboxen.

(0022) It has thus been shown that carbon nanotubes provide another very useful new substrate for the collection of CW-related target compounds associated with airborne weapons of mass destruction (WMD) at dilute concentrations in air samples. The carbon nanotubes function equally well in aqueous samples. Also, when the carbon nanotubes are incorporated in new collection tools, the nanotubes will be potentially very useful in nonproliferation applications. Since the carbon nanotubes-coated materials possess high collection efficiencies, in addition to CW-related compounds, they can be utilized for environmental clean-up, disease state diagnosis, high explosive detection, process control, environment monitoring, and chemical synthesis.

(0023) While particular embodiments and fabrication approaches, along with specified materials and parameters have been set forth to exemplify and teach the principals of the invention, such are not intended to be limiting. Modifications and changes may become apparent to those skilled in the art, and it is intended that the invention be limited only by the scope of the appended claims.

WHAT IS CLAIMED IS

1. In a collector for collecting and concentrating organic compounds, the improvement comprising:
a carbon nanotubes material as the collector.
2. The improvement of Claim 1, wherein said carbon nanotube material is coated on a support member.
3. The improvement of Claim 2, wherein the material is coated by uniform airbrushing with a solution containing carbon nanotubes.
4. The improvement of Claim 2, wherein the material is coated by uniformly suspending carbon nanotubes in a solvent containing a binder, and spraying the solvent using ultrasonic impulses.
5. The improvement of Claim 4, wherein the binder is an oryanosilane.
6. The improvement of Claim 1, wherein said carbon nanotube material is composed of carbon nanotubes having a diameters of about 2nm and a length of at least one hundred micrometers.
7. The improvement of claim 5, wherein the oryanosilane is polydimethylsilane.
8. A method for fabricating a carbon nanotube collector for airborne organic compounds, comprising:
providing a quantity of carbon nanotubes, and coating the carbon nanotubes on a substrate.
9. The method of Claim 8, wherein coating is carried out by airbrushing the member with a solution containing the carbon nanotubes.
10. The method of Claim 8, wherein coating is carried out by spraying a solution containing the carbon nanotubes in a binder using ultrasonic impulses to the spray apparatus.
11. The method of Claim 10, additionally including uniformly suspending the carbon nanotubes in the binder.

12. The method of Claim 11, wherein the binder is composed of oryanosilane.

13. The method of Claim 12, wherein the oryanosilane is polydimethylsilane.

14. The method of Claim 9, additionally including forming the quantity of carbon nanotubes.

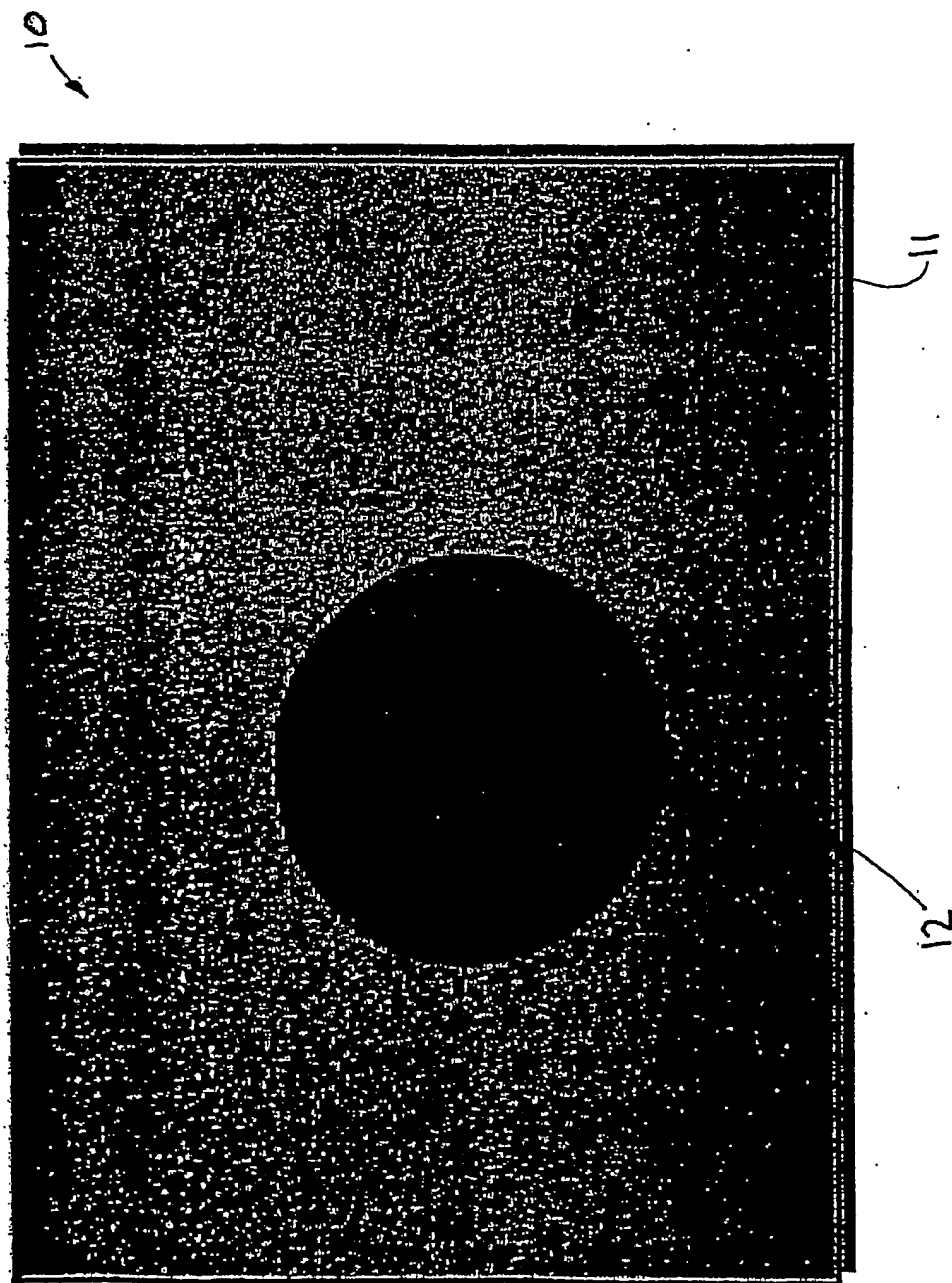
15. The method of Claim 14, wherein the carbon nanotubes are formed to have a diameter of about 2nm and a length of a number of hundred micrometers.

16. A collector for chemical warefare-related materials which includes carbon nanotubes.

17. The collector of Claim 16, wherein said carbon nanotubes are coated on a member to be exposed to vapors, aqueous material, and waste systems.

18. The collector of Claim 16, wherein said chemical warefare-related materials include vapors of compounds selected from the group consisting of dimethylmethylphosphonate, diisopropylaminoethanol, and diisopropylmethylphosphonate.

19. The collector of Claim 16, wherein said carbon nanotubes have a diameter of about 2nm and a length of several hundred micrometers.



SUBSTITUTE SHEET (RULE 26)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 December 2002 (19.12.2002)

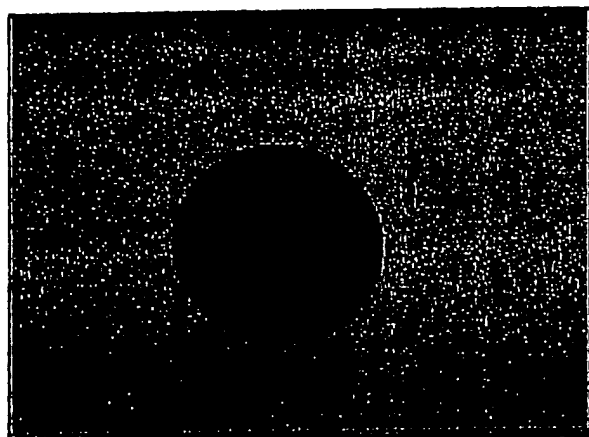
PCT

(10) International Publication Number
WO 02/100775 A3

- (51) International Patent Classification⁷: C01B 31/02, B01D 53/04, B01J 20/20, 20/28, C02F 1/28 (74) Agent: THOMPSON, Alan, H.; P.O. Box 808, L-703, Livermore, CA 94551 (US).
- (21) International Application Number: PCT/US02/18669 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 11 June 2002 (11.06.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/298,602 13 June 2001 (13.06.2001) US
10/163,720 5 June 2002 (05.06.2002) US
- (71) Applicant: THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 1111 Franklin Street, Oakland, CA 94607-5200 (US).
- (72) Inventors: TILLOTSON, Thomas, M.; 210 E. Berverdor Avenue, Tracy, CA 95376 (US). ANDRESEN, Brian, D.; 1075 Alison Circle, Livermore, CA 94550 (US). AL-CARAZ, Armando; 592 Chardonnay Drive, Fremont, CA 94539 (US).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report

[Continued on next page]

(54) Title: CARBON NANOTUBE COATINGS AS CHEMICAL ABSORBERS



(57) Abstract: Airborne or aqueous organic compound collection using carbon nanotubes. Exposure of carbon nanotube-coated disks to controlled atmospheres of chemical warfare (CW)-related compounds provide superior extraction and retention efficiencies compared to commercially available airborne organic compound collectors. For example, the carbon nanotube-coated collectors were four (4) times more efficient toward concentrating dimethylmethyl-phosphonate (DMMP), a CW surrogate, than Carboxen, the optimized carbonized polymer for CW-related vapor collections. In addition to DMMP, the carbon nanotube-coated material possesses high collection efficiencies for the CW-related compounds diisopropylaminoethanol (DIBA), and diisopropylmethylphosphonate (DIMP).

WO 02/100775 A3



(88) Date of publication of the international search report:
20 February 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/18669

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B31/02 B01D53/04 B01J20/20 B01J20/28 C02F1/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; WADA, SATORU ET AL: "Air purification filtering unit" retrieved from STN Database accession no. 131:148448 CA XP002215311 abstract	1,2,8, 16,17
A	& JP 11 221414 A (MITSUBISHI ELECTRIC CORP., JAPAN) 17 August 1999 (1999-08-17) --- -/--	6,9,10, 19

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

1 October 2002

Date of mailing of the international search report

18/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rigondaud, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/18669

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; ZINOV'EV, A. P. ET AL: "Method of purification of highly polluted water" retrieved from STN Database accession no. 136:107110 CA XP002215312 abstract	1,16
A	& RU 2 159 743 C (UFIMSKII GOSUDARSTVENNYI NEFTYANOI TEKHNICHESKII UNIVERSITET, RUSSIA) 27 November 2000 (2000-11-27) ---	6,8, 17-19
X	RICHARD Q. LONG ET AL.: "Carbon nanotubes as superior sorbent for dioxin removal" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol. 123, no. 9, 7 March 2001 (2001-03-07), pages 2058-2059, XP002215310 AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC., US ISSN: 0002-7863 the whole document	1,16
A	---	8,17-19
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 10, 30 November 1995 (1995-11-30) & JP 07 185327 A (NEC CORP), 25 July 1995 (1995-07-25) abstract	1,16
A	---	6,8, 17-19
P,X	WO 02 32558 A (NOACK ANDREAS) 25 April 2002 (2002-04-25) claims 1,3,17,28 page 38, line 9 -page 39, line 16 ---	1,16
A	DE 198 26 681 A (MARQUARDT NIELS) 23 December 1999 (1999-12-23) ---	
A	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; NAKAMURA, NAOKI: "Gas-adsorbing materials and manufacture of same." retrieved from STN Database accession no. 134:73515 CA XP002215313 abstract & JP 2001 000860 A (TOYOTA MOTOR CORP., JAPAN) 9 January 2001 (2001-01-09) ---	
	--- -/--	

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 02/18669

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 648 569 A (REUTTER DALLAS WESLEY ET AL) 15 July 1997 (1997-07-15) the whole document _____	

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/18669

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 11221414	A	17-08-1999	NONE	
RU 2159743	C	27-11-2000	RU 2159743 C1	27-11-2000
JP 07185327	A	25-07-1995	JP 2710198 B2	10-02-1998
WO 0232558	A	25-04-2002	DE 10051910 A1	02-05-2002
			AU 1056002 A	29-04-2002
			WO 0232558 A1	25-04-2002
DE 19826681	A	23-12-1999	DE 19826681 A1	23-12-1999
JP 2001000860	A	09-01-2001	NONE	
US 5648569	A	15-07-1997	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.